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A Relativistic 4-Component Multi-Reference Coupled Cluster Method. Application to the CsLi Molecule

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Spectroscopic accuracy in electronic-structure calculations on heavy-element molecules requires a simultaneous and high-level treatment of electron correlation and contributions owing to special relativity. We present a general-order multi-reference coupled-cluster approach in the 4-component relativistic framework and its large-scale application to the spectroscopic properties of the CsLi molecular ground state. Using different relativistic Hamiltonians and varying levels of electron correlation, we find that electron correlation leads to a larger bond contraction than inclusion of "scalar" relativistic effects. By considering full iterative Triple excitations in the coupled cluster treatment, we attain benchmark precision for the bond length and the harmonic vibrational frequency in the $^1\Sigma$ ground state.

1 Introduction

The smallest building blocks of matter of interest in chemistry and physics are comprised — at the level above elementary particles — by atoms and small molecules. A detailed understanding of these systems is highly desirable, both for the sake of knowledge about the small systems themselves as well as the implications of this knowledge for larger molecules. A "small" molecule will be understood as consisting of not more than six or seven atoms.

The first and foremost piece of information about atoms and small molecules relevant to chemistry and molecular physics is delivered by the investigation of the electron "cloud" surrounding the nuclei, the electronic structure. The theoretical framework for such investigations is provided by quantum mechanics, and the quantum mechanical methodology for carrying out the relevant calculations is at the heart of quantum chemistry.

The accurate quantum chemical treatment of molecules containing heavy atoms from the 5th period of the periodic table and beyond puts high requirements on the applied methods. In particular, the precise determination of molecular spectra and properties, the understanding of reactions etc. crucially depends on the description of electron correlation which for heavy elements necessarily includes an adequate consideration of special relativity. The focus of our applied work lies on the precise determination of spectroscopic properties of small molecules containing heavy elements. This includes, e.g., high-precision calculations of molecular equilibrium bond lengths, harmonic vibrational frequencies, and dissociation energies within or even better than chemical accuracy (1 kcal/mole for energy differences).

To obtain high precision in properties, the quantum chemical treatment must go beyond Hartree-Fock theory, i.e. a mean-field approach to the electron-electron interaction.

Electron correlation must be described as precisely as possible. Alongside with improving computer technology and increasing system size of standard molecular applications, the coupled-cluster (CC) method has established itself as the most efficient *ab initio* method for the assessment of a large fraction of the correlation energy[1,2]. The exponential (or product) parameterization of the wave function leads to size-extensive model theories — i.e. the correlation energy scales correctly with the number of interacting particles — already at the level of truncated cluster expansions. Furthermore, the exponential *Ansatz* accounts for a compact representation of the wave function thus outperforming e.g. configuration interaction (CI) theory at a given excitation level.

Non-relativistic implementations of the CC method with the cluster excitation operator acting on a single-determinant reference (SRCC) have become widely used and are available in many quantum chemistry program packages (e.g.[3–5]). The SRCC method is a valid and good approach in situations where the wave function of the system is dominated by the single reference, e.g. the Hartree-Fock state, which is the case in many molecules of chemical interest. It lacks applicability or becomes less efficient, though, when a given state of interest is described by several electronic configurations of similar weights. This occurs in typical open-shell systems, like compounds of the transition metal, lanthanide, and actinide atoms[6,7], in bond-breaking regions of molecules with multiple bonds[8], or in the calculation of excited states[9].

The most elegant way to overcome these difficulties is to re-define the reference space in terms of a model space containing multiple determinants. These multi-reference coupled-cluster (MRCC) methods are generally demanding both on the implementational as well as the computational side and have therefore not become standard tools of quantum chemistry, yet. A type of these are the state-selective or state-specific (SS) methods, where a single reference comprised by a multideterminantal expansion with fixed weights is employed[10,11].

Relativistic generalizations of the CC method have also been explored in the last decade. The problematic objective here consists in the inclusion of internal magnetic couplings, in particular the spin-orbit interaction. As spin and orbital angular momenta are coupled, the concomitant quantum numbers lose relevance, and the methods require severe structural modifications. The earlier SR implementations of closed- and open-shell type[12–15] using the no-pair Dirac-Coulomb Hamiltonian have recently been succeeded by Fock-Space CC implementations[16,17] capable of simultaneously determining potential surfaces for different oxidation states and electronic levels of molecules[9]. The treatment of general open-shell systems is still impossible with this method, as the same set of molecular orbitals is used for all ionization levels of the treated system, which hampers convergence when Fock space sectors higher than 2/-2 need to be included.

2 Method

The goal of our project is to obtain a *universally applicable* coupled cluster method which suffers no limitations due to the number of open shells of a system state or the importance of relativistic contributions and possible non-additivity of relativistic contributions and electron correlation. The most rigorous theoretical framework to account for all these relativistic effects is Dirac's relativistic quantum mechanics. Here, the Hamiltonian and the wave function obtain 4-component form, the additional components owing to the descrip-

tion of anti-matter, e.g. positrons. In 4-component relativistic theory, scalar relativistic and magnetic effects are intertwined and consistently included. Our approach is based on 4-component theory and approximative ansatzes within the 4-component framework, both with respect to method development and application, and solutions are obtained to the Dirac (-Coulomb), not the Schrödinger equation.

The precursor implementation we set out from is the general CI and CC program LUCIA[18,19]. This very general approach to the CC method belongs to the category of state-selective multi-reference CC techniques and allows for including cluster operators of arbitrary excitation level. Its generality further rests upon the concept of generalized active spaces (GAS), where the occupied and virtual orbital spaces are subdivided into a number of subspaces with defined occupation constraints, thus representing a multi-reference expansion of the wave function. The reference model space is therefore comprised by a (CAS) expansion onto which the cluster operators act. In contrast to single-reference CC, the excitation manifold is extended to include excitations also from the additional reference functions up to the specified level of cluster expansion.

The following hierarchical tree shall help provide a complete overview of the methodology we have recently implemented in a local version of the quantum chemistry program package DIRAC[20] and its interrelations:

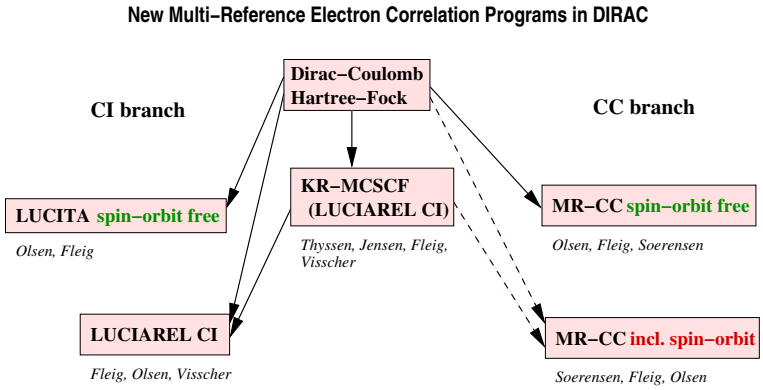

Figure 1. An overview of the new relativistic 4-component electron correlation programs in DIRAC and the main authors of the modules.

We have completed the spin-orbit free implementation of the multi-reference CC method within this framework, and report applications in the following section. This allows for electronic structure calculations on systems where spin-orbit interaction does not affect properties severely, but where the so-called “scalar relativistic” effects need to be accounted for. The latter lead to orbital contractions and self-consistent decontractions and thus modify the electron density of the system, strongly affecting properties in heavy-element systems. In the 4-component framework, scalar relativistic effects are conveniently treated through the spin-free Dirac operator[21]. Our implementation generally treats relativistic contributions and electron correlation simultaneously and on the same footing.

The full spin-orbit MR-CC code is currently being implemented by modification of the fully relativistic CI program LUCIAREL[22,23] which is invoked from the new 4-component multi-configuration self-consistent-field (MCSCF) program (KR-MCSCF)[23,24].

3 Application

3.1 Motivation

A number of small molecules containing heavy atoms have electronic ground states with very small contributions from spin-orbit coupling. This is the case in diatomic molecules with Σ states, examples of which are the ground states of the group 1 and group 2 diatomic compounds ($\mathrm{KCs}, \mathrm{NaCs}, \mathrm{Rb_2}, \mathrm{Cs_2}, \mathrm{BaLi}$ and the like) and some molecules formed from group 1 and lanthanide atoms (e.g. RbYb). The ultracold formation of these molecules[25] and their capture into optical and magnetic traps[26] is of particular interest in the study of Bose-Einstein condensation[27]. In the ground states of these molecules the relativistic effects are typically dominated by so-called scalar contributions such as mass-velocity and the Darwin term in the molecular Hamiltonian. These effects cannot be neglected in any heavy-element calculation since they are decisive for the determination of the shape and spatial extent of the orbitals and therfore also the bonding situation in molecules. The relatively weak bonding in such molecules also calls for an extensive treatment of dynamic electron correlation as insufficiencies in the correlation treatment are likely to lead to large errors in spectroscopic properties.

3.2 Problem and Approach

The chemical bond in the CsLi molecule can be reasonably described by considering only the σ bond formed from the 6s orbital on Cs and the 2s on Li, resulting in a $^1\Sigma^+$ ground state. Correlation of the close-lying 5p and 5s orbitals (10 electrons in total) of Cs will give a significant improvement on the desription of the bond. Further improvement is expected when correlating the outer core 4d electrons of Cs and the 1s electrons of Li (22 electrons in total) and going to higher excitation levels.

A series of calculations using our new implementation within the DIRAC program package[20] has been performed[28]. Our goal is to determine with highest precision the contributions of scalar relativity, spin-orbit coupling, and electron correlation to spectroscopic properties of the CsLi molecule. For this, we use a Levy-Leblond (non-relativistic), spin-orbit free and the Dirac-Coulomb Hamiltonian which includes all leading relativistic terms. The calculations are carried out with large uncontracted basis sets ($\{24\mathrm{s}18\mathrm{p}13\mathrm{d}3\mathrm{f}\}$ functions on Cs and $\{11\mathrm{s}5\mathrm{p}2\mathrm{d}1\mathrm{f}\}$ functions on Li).

3.3 Results

Results for different levels of electron correlation ((0) Hartree-Fock, 10-electron coupled cluster, 22-electron coupled cluster) are compiled in table 1.

The most striking overall trend is the large bond contraction upon correlating the electrons. Our finding shows that the decrease in bondlength stems from moving density from the predominantly delocalized bonding orbital to the more diffuse and localized low-lying

Method	corr. el.	R_e[Å]	ω_e [cm^{-1}]	D_e [eV]
DCHF-SF	0	3.9092	173.868	-
DCHF	0	3.9094	173.833	-
CCSD-LL	10	3.7313	184.561	0.8480
CCSD-SF	10	3.6700	187.102	0.8257
CCSD	10	3.6688	187.277	0.8382
MRCCSD(2in2)-SF	10	3.6699	186.333	0.7916
CCSD(T)-SF	10	3.6419	186.508	-
CCSD(T)	10	3.6405	186.605	-
CCSDT-LL	10	3.7025	183.862	0.7665
CCSDT-SF[a]	10	3.6416	186.205	0.7432
CCSDT-SF	10	3.6423	186.358	
CCSD-LL	22	3.7196	185.196	0.9001
CCSD-SF	22	3.6562	187.935	0.8798
CCSD	22	3.6560	188.372	0.8806
CCSD(T)-SF	22	3.6242	187.294	-
CCSD(T)	22	3.6232	187.385	-
CCSDT-SF[a]	22	3.6225	186.522	0.7522
CIPSI[b]		3.615	187.1	
MELD[c]		3.65	183	0.72
CIPSI[d]		3.604		0.717

Table 1. Spectroscopic properties of CsLi in its $^1\Sigma$ ground state at various correlation levels and using different Hamiltonians. LL denotes the Levy-Leblond, SF the spin-orbit free Hamiltonian. MR characterizes a multi-reference CC expansion.
[a] Cutoff for virtuals at 6.2 a.u., [b] Reference[29], [c] Reference[30], [d] Reference[31]

$3p_x$ and $3p_y$ orbitals on Li but not the $3p_z$ thereby making the molecule more ionic and leading to bond contraction. This is found by specifying various active orbital spaces (GAS). As expected, the bond also becomes considerably shorter when including scalar relativistic effects since the predominantly bonding 6s orbital on the Cs atom is contracted. The inclusion of spin-orbit coupling, on the other hand, has virtually no effect on any of the properties here. This is clearly visible by comparing the CCSD-SF and CCSD calculations which refer to the fully relativistic Dirac-Coulomb Hamiltonian. The effect of outer core correlation in general is small compared to the correlation effect as such (less than 10% of the latter) though not neglible and about one third of scalar relativistic contributions. It is just slightly smaller than increasing the excitation level from CCSD-SF (Singles and Doubles) to CCSDT-SF (Singles, Doubles, and full iterative Triples). A multi-reference expansion improves results especially on dissociation, as the separated atoms and the bonded molecule are described at better balance than in single-reference treatments.

Conclusively, an extensive correlation treatment in this weakly bound molecule is very important to approach spectroscopic accuracy. The reported reference calculations have

been carried out using effective core potentials and configuration interaction for describing electron correlation. No experimental results are available for direct comparison, but we draw confidence for the accuracy of our calculations from the systematic study of all relevant contributions and the stepwise improvement of the computational approach. We are currently investigating the convergence of the dissociation energy with extensive MR calculations correlating 22 electrons.

4 Concluding Remarks

The coupled cluster implementation we are pursuing here opens the possibility of the high-precision calculation of molecular spectroscopic (and electric) properties due to the arbitrary cluster excitation level and the possibility of using multi-reference expansions. The largest calculation reported here (CCSDT-SF 22) includes roughly 100 million cluster amplitudes and requires significant amounts of machine core memory. JUMP provides both fast processors for running large-scale calculations of this quality as well as ample memory for storing the required intermediate quantities such as amplitude vectors, molecular integrals, etc.

These requirements will become even more important when we have completed our initial implementation including spin-orbit terms. We plan to apply the new program in electronic-structure calculations of actinide-containing molecules, in particular small uranium and plutonium compounds with several unpaired electrons. Currently, there is no quantum-chemical methodology available for the treatment of such molecules which may guarantee chemical accuracy for the properties we are interested in.

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